Thermal and Mechanical Characterization of ViaLux™ 81: A Novel Epoxy Photo-Dielectric Dry Film (PDDF) for Microvia Applications

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***Abstract*—Multilayered high density interconnect (HDI) processing on organic substrates typically introduces warpage and residual stresses. The magnitude of the warpage and the residual stresses depends on, among other factors, the processing temperatures and the thermomechanical properties of the dielectric and substrate materials. In this work, a prospective epoxy-based dielectric material for such sequentially built up (SBU) high density-interconnect printed wiring boards (HDI-PWB) is considered. The polymer is a photo-dielectric dry film (PDDF) material called ViaLux™ 81, which exhibits a complicated curing behavior due to the long lifetime of the cationic photoinitiators generated by ultraviolet (UV) exposure. The objectives of this work are**

1) **to conduct differential scanning calorimetry (DSC) experiments and develop a cure kinetics model;**
2) **to develop a cure shrinkage model based on thermal and chemical shrinkage experiments;**
3) **to determine the thermomechanical properties of partially and fully cured Vialux™ 81 dry film.**

All of these experimental characterizations are necessary to select suitable process parameters and to obtain a consistent product with the desired physical and mechanical properties.

***Index Terms*—Cure kinetics, differential scanning calorimetry (DSC), dynamic mechanical analysis, high-density wiring, interlayer dielectric, microvias, substrate processing.**

I. Introduction

As the semiconductor industry continues its relentless pace toward reduced feature sizes, increased functionality and improved performance at lower costs, the traditional PWB industry needs to adopt innovative technologies to meet the IC packaging challenges. A viable solution to realize higher levels of silicon integration is to employ HDI-PWB's with sequentially-built-up (SBU) microvia technology. Besides meeting the fine pitch requirements, the use of smaller microvias to connect the inner circuitry results in

1) a significant reduction in board real estate consumption;
2) better signal integrity due to the reduction in simultaneous switching noise.

One option to create the microvias is to first laminate a photo-dielectric dry film (PDDF) material on a base substrate, and then mass fabricate the microvias (interconnect vias) by UV irradiation. This is followed by post-exposure thermal bake, development in an appropriate solvent and a final thermal bake to cure the material. Subsequently, an additive or subtractive electroless and/or electrolytic plating process may be used to metallize the vias and the lines. Sequential repetition of alternate layers of dielectric and metallization results in a multilayered HDI structure ([2], [3]). A significant challenge to the widespread application of HDI technology is the extensive material chemistry, physics and interactions issues that have to be considered, and the direct impact of these material issues on the thermomechanical integrity of the HDI substrate. Careful selection and processing of the dielectric material is important to ensure HDI reliability and functionality [5].

In this paper, a prospective interlayer dielectric material for such HDI applications, ViaLux™ 81, is considered. ViaLux™ 81 is an epoxy-based photo-definable dry film material, which is amenable to lamination on a substrate in a vacuum laminator. The dry film format is advantageous, as it allows a wide range of thicknesses, tighter thickness control, a high degree of planarity and a solvent-free coating without pinhole defects ([6]).

The objectives of this work are three-fold:

1) to conduct differential scanning calorimetry (DSC) experiments and develop a cure kinetics model;
2) to develop a cure shrinkage model based on thermal and chemical shrinkage experiments;
3) to determine the thermomechanical properties of partially and fully cured Vialux™ 81 dry film.

An understanding of the degree-of-cure (DOC) evolution is useful because this knowledge can be used to optimize the curing schedule of Vialux™ 81 for a wide range of potential applications, to understand structure-property relationships, to control the stresses induced during fabrication, and to enhance the thermomechanical reliability during further qualifications. However, the lack of material composition information makes the kinetic analysis presented here strictly phenomenological in nature.

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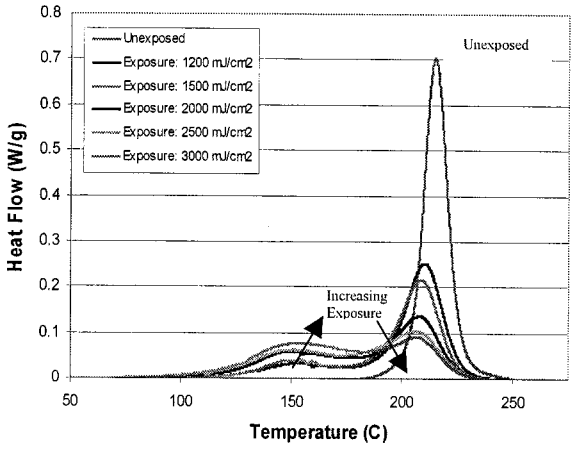


Fig. 1. Effect of varying exposure dose on uncured samples.

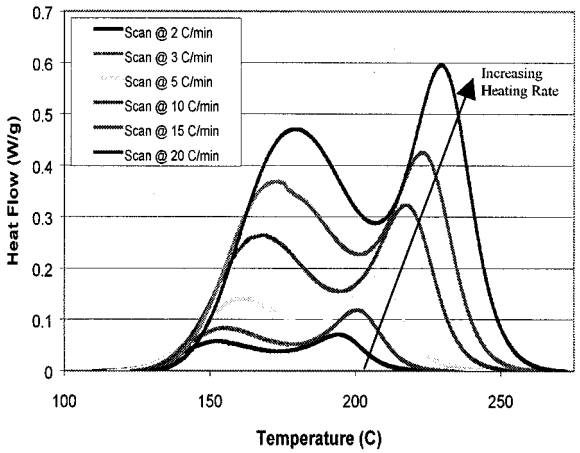


Fig. 2. Dynamic DSC data (baseline corrected) at multiple heating rates (explosure $= 2000$ mJ/cm^2).

Earlier work by the authors on this material described a complex curing mechanism, with two distinct curing peaks observed in dynamic DSC scan experiments ([4]). The two peaks were caused due to the long lifetime of the photoinitiator catalyst, and could not be separated at lower heating rates. The first peak was attributed to UV irradiation-induced photolytic decomposition of the cationic photoinitiator to create a superacid (H^+), which promoted ring opening polymerization of the epoxy group. The second peak was due to the thermal decomposition of the photoinitiator to produce additional superacid, which promoted additional epoxy polymerization.

Initial dynamic DSC scans at 5 °C/min on several uncured samples irradiated with varying UV exposure doses (1200–3000 mJ/cm^2) indicated that shorter cure cycle times were possible with increased exposure doses (Fig. 1). Therefore, an exposure dose of 2000 mJ/cm^2 was selected in all the subsequent experiments, as this resulted in a significant reduction in the post-exposure enhancement bake and final thermal bake time of the dielectric at the expense of a marginal increase in UV exposure time.

To develop the cure kinetics model, a series of isothermal and dynamic DSC experiments were conducted on samples exposed to 2000 mJ/cm^2. While the dynamic DSC scans at multiple heating rates revealed a two-stage curing mechanism, the heat flow exotherms from isothermal DSC experiments showed a rapid reaction rate at the beginning with only a single peak. Therefore, to capture the complexity of the process, the faster multiple heating rate DSC experiments were used to predict the degree-of-cure (DOC) evolution (Fig. 2). A "model-free" method suggested by [11] was implemented, which required information only about the cure-dependence of the activation energy ([4]). Excellent agreement was observed for the heating rate experiments, but the method was inadequate for predicting the DOC evolution under isothermal conditions. Therefore, a modified auto-catalytic model with temperature-dependent kinetic parameters has been developed based on isothermal DSC data.

In addition, to aid the study of residual stresses, pressure-volume-temperature (PVT) experiments were conducted to predict the volume changes during cure. The volumetric coefficient of thermal expansion (CTE) and bulk modulus were also determined from PVT experiments on fully cured samples. In conjunction with the in-plane CTE evaluation from TMA experiments, the isotropy of the thin films was established. Finally, dynamic mechanical analysis (DMA) was done to assess the glass transition temperature (T_g) of samples with different DOCs, and to determine the cure-dependent viscoelastic stress relaxation modulus.

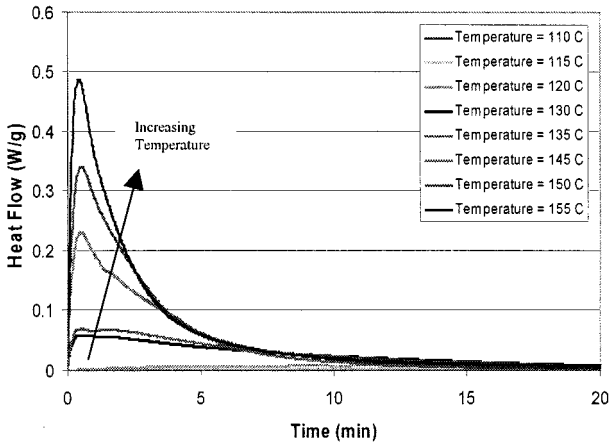
II. Cure Kinetics Modeling

In this section, a predictive cure kinetics model for the evolution of degree-of-cure (DOC) with time and temperature under any arbitrary temperature–time loading profile has been developed, based on isothermal DSC experiments.

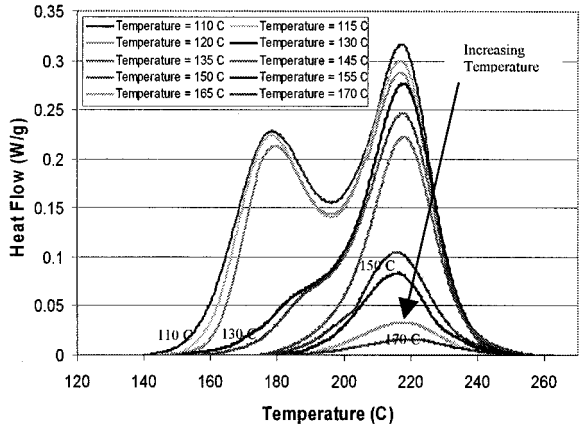
A. Isothermal DSC Experiments

The isothermal DSC measurements were performed in a TA Instruments 2920 MDSC™ (Modulated Differential Scanning Calorimetry) instrument. Due to the presence of some solvents in the material, smaller sample sizes of 5–8 mg were used in hermetically sealed aluminum pans and in a nitrogen purge gas environment. The isothermal experiments were done from 110 °C to 175 °C in 5 °C increments for a duration of 60 min. A subsequent dynamic scan was done at 10 °C/min on each of these samples to determine the residual heat of reaction, if any.

Fig. 3(a) shows the heat flow data for samples cured at different isothermal temperatures. The residual exotherms for the isothermally cured samples are obtained from the subsequent DSC scan, and is illustrated in Fig. 3(b). As can been observed from the subsequent DSC scan data in Fig. 3(b), isothermal curing is incomplete up to 170 °C. However, when the isothermal cure temperature was increased to 175 °C, no residual exotherm was obtained indicating complete cure of the material at 175 °C. As has been reported earlier in [4], these results suggest that a cure duration of approximately 15 minutes at temperatures above 165 °C could result in a DOC greater than 90%. This implies that faster fabrication is possible with either rapid thermal curing (RTC) equipment or continuous belt furnaces.



(a)



(b)

Fig. 3. (a) Isothermal DSC data (baseline corrected) at different temperatures (exposure $= 2000$ mJ/cm^2) [abscissa scaled for clarity] and (b) subsequent DSC scan data (baseline-corrected) of the isothermally cured samples (Exposure $= 2000$ mJ/cm^2).

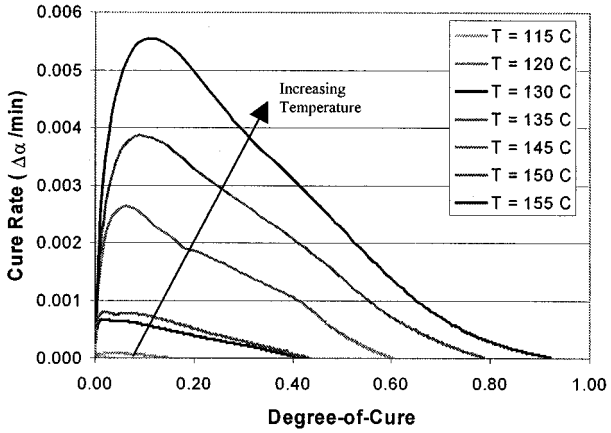


Fig. 4. Cure rate versus DOC from isothermal experimental data.

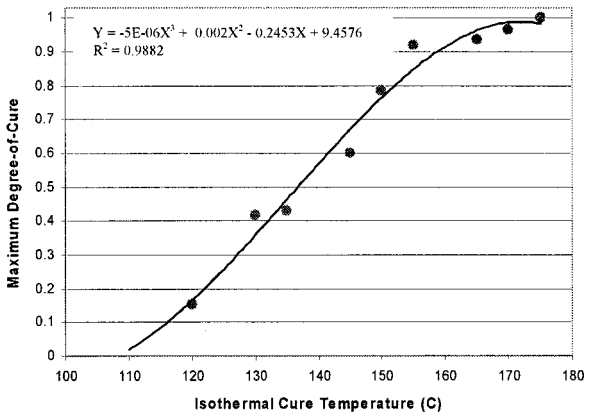


Fig. 5. Maximum DOC achieved at various isothermal cure temperatures.

B. Cure Kinetics Model

The isothermal data shown in Fig. 3(a) was used to develop a cure kinetics model. Significant heat flow losses could occur at the start in such experiments when the sample is trying to equilibrate at the prescribed isothermal temperature, as well as near the apparent completion when the reaction rate falls below the sensitivity of the calorimeter ([1]). With this knowledge, as well as from the fact that very rapid curing rates exist at the beginning at increased cure temperatures, only the isothermal data at 130, 135, 145, 150, and 155 °C were considered to develop the model. The plot of cure rate with DOC at these temperatures, as illustrated in Fig. 4, clearly shows that the cure rate increases with increasing temperature, and the DOC at the maximum cure rate also increases with an increase in the curing temperature. The latter implies that the activation energy for the curing process is not a constant. An additional observation of importance is that with an increase in the isothermal cure temperature, the maximum DOC achieved at that temperature increases (see Fig. 5). Full cure is attained only at temperatures of about 175 °C, as was observed earlier in Section II-A.

The basic rate equation which expresses the reaction rate as a function of time or temperature with conversion [1] is

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = Ae^{-\mathrm{EIRT}}f(\alpha) \tag{1}$$

where

α	degree-of-cure;
$f(\alpha)$	reaction model;
k	rate constant;
A	pre-exponential or frequency factor;
E	activation energy;
R	gas constant;
T	temperature;
t	time.

The two reaction models that are used most commonly for thermosetting systems are the nth order, where $f(\alpha) = (1-\alpha)^n$ [8], or autocatalytic models, where $f(\alpha) = \alpha^m(1-\alpha)^n$ [8].

Fig. 4 implies that an autocatalytic model of the form $f(\alpha) = \alpha^m(1-\alpha)^n$ might provide a suitable fit to the data. An intrinsic property of the autocatalytic model is that the maximum cure rate occurs at a fixed degree-of-cure $\alpha^* = m/(m+n)$ [10]. However, since the maximum DOC achieved at the various isothermal cure temperatures is different, a modified autocatalytic model is developed to account for the temperature-dependence of the maximum DOC at different isothermal cure temperatures, as shown in Fig. 5 ([9])

$$\frac{d\alpha}{dt} = k[T]\alpha^{m[\mathrm{T}]}(\alpha_{\max}[T]-\alpha)^{n[\mathrm{T}]}. \tag{2}$$

To calculate the kinetic parameter n, (2) is rewritten in the form

$$\ln\left[\frac{d\alpha}{dt}\right] = \ln[K] + n\ln\left[\alpha^p(\alpha_{\max} - \alpha)\right] \tag{3}$$

where $p = m/n$, is the kinetic parameter ratio, which can be re-expressed in terms of α^* as $p = \alpha^*/(\alpha_{\max} - \alpha^*)$. The kinetic parameter n is determined from the slope of the linear dependence of $\ln[d\alpha/dt]$ versus $\ln[\alpha^p(\alpha_{\max} - \alpha)]$ for each of the temperatures. Thereafter, m is calculated from $p = \alpha^*/(\alpha_{\max} - \alpha^*)$, and the rate constant K is computed by transposing the reaction model to the left hand side in (3). All the results for the temperature-dependent kinetic parameters are summarized as

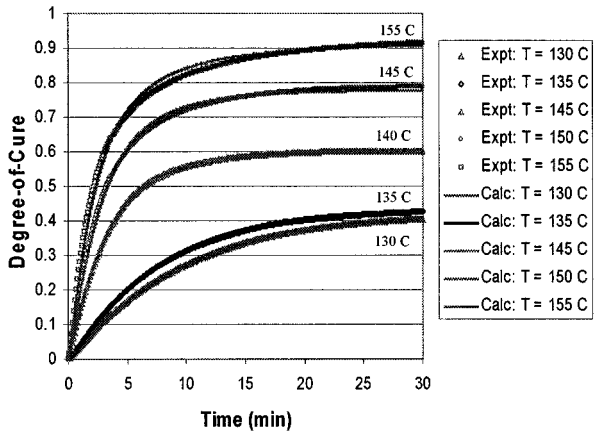
$$\begin{aligned}
\alpha_{\max}[T] &\quad -0.000\,005T^3 + 0.001\,998\,8T^2 \\
&\quad -0.2453T + 9.4576 \\
m[T] &\quad 0.0041T - 0.4553 \\
n[T] &\quad 0.0224T - 2.0608 \\
K[T] &\quad \exp\left[\frac{23.1704 - 11\,864.2699}{T}\right] \\
&\quad A\exp\left(\frac{-98.6395}{RT}\right).
\end{aligned} \tag{4}$$

Solution of the cure rate equation using the 4th order Runge Kutta method yields the DOC evolution with time. Excellent agreement is evident at the selected isothermal temperatures from Fig. 6(a).

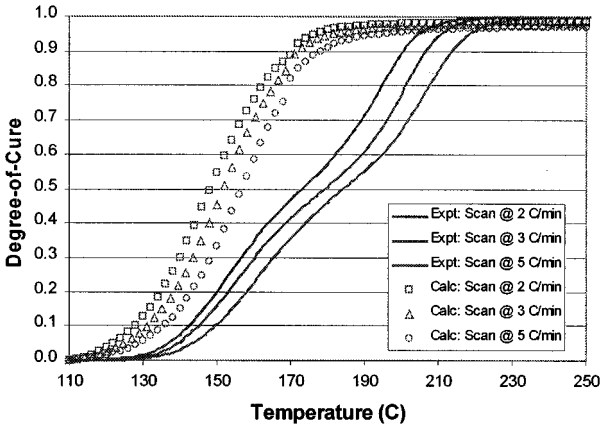
However, there does exist some deviation in the DOC evolution with temperature for the heating rate experiments [see Fig. 6(b)]. This deviation is primarily due to the under-prediction of the activation energy, which may be calculated from the $K[T]$ expression in (4) to be 98.64 kJ/mol. Given the complex curing behavior and the solvent effects in the material which affect the DSC thermograms, this discrepancy was manually corrected by increasing the activation energy in (4) to 124 kJ/mol, which is equivalent to shifting the calculated curves to the right. This modification yields fairly accurate results for the heating rate experiments for temperatures until 175 °C, which is the upper temperature limit to achieve full cure of the Vialux™ 81 material. However, the discrepancy at higher temperatures cannot be avoided for both isothermal and dynamic heating conditions, since the modified autocatalytic model allows only a single activation energy for the entire process [10].

C. Model Validation

In this section, the DOC evolution for a complicated cure schedule with a combined heating rate and isothermal segment is presented. A DSC experiment was conducted with an initial heating rate segment of 10 °C/min from room temperature to 170 °C, followed by an isothermal hold segment at 170 °C for 30 min. The DOC evolution with time was calculated using the modified autocatalytic model. As shown in Fig. 7, fairly good agreement in observed between the calculated and experimental results. This gives us a fair deal of confidence in predicting the cure kinetics under arbitrary cure schedules using the modified autocatalytic model in (3) and (4).



(a)



(b)

Fig. 6. (a) Isothermal DSC data: Comparison of experimental and calculated DOC with time and (b) dynamic DSC data: comparison of experimental and calculated DOC with temperature.

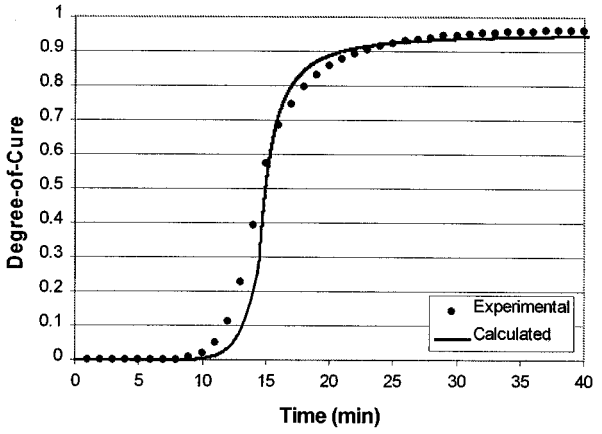


Fig. 7. Model validation: 10 °C/min heating rate from 25 °C to 170 °C, followed by 30 min hold at 170 °C.

III. Cure Shrinkage Modeling

Polymerization shrinkage of thermosetting polymers can be a major problem in reactive processing, as it might lead to internal stresses, poor surface quality, warpage and in extreme cases, the formation of cracks. The polymerization shrinkage data can be measured only by the application of dilatometry or measurement of the monomer and polymer densities.

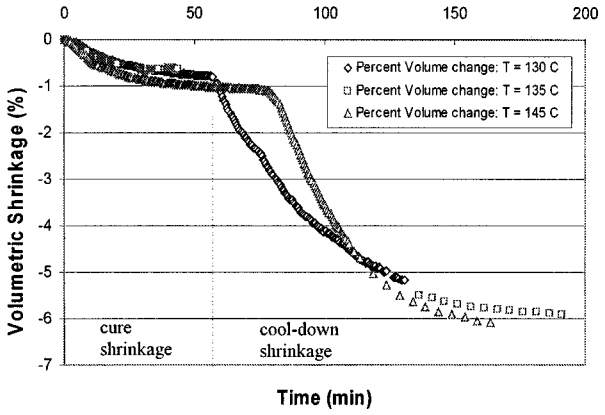


Fig. 8. Volume change during isothermal cure.

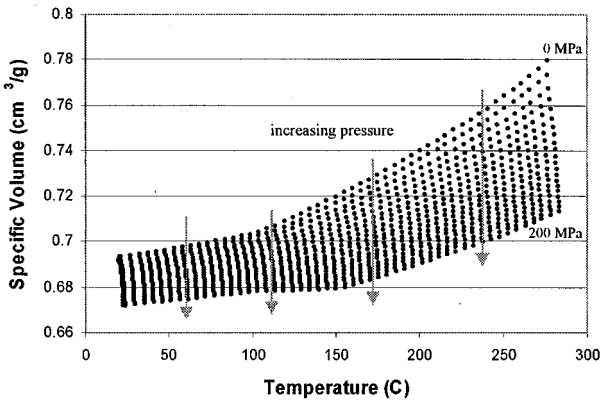


Fig. 9. Cross-plotted isobars from 0–200 MPa in 10 MPa increments.

In this work, the volumetric dilatometer used to assess the cure shrinkage was the GNOMIX™, Inc. PVT apparatus ([12], [13]). Typical sample sizes vary from 1–2 g. The volume of the vessel was approximately 15.8 cm^3, and that of the sample chamber was about 3.2 cm^3. The sample and the confining fluid (Hg) were contained in a rigid sample cell, one end of which was closed off with a flexible metal bellow. To ensure reliable measurements, a minimum hydrostatic pressure of 10 MPa was always maintained on the sample. This was necessary to prevent the evaporation of Hg (which boils at 357 °C at atmospheric pressure), and to suppress any gases which might be present in the dilatometer after filling Hg. Furthermore, to maintain the hydrostatic pressure state at all times during densification, the sample was placed in a 1 mil thick open cup formed of thin nickel foil ([7]). The volume of the vessel (Hg+ sample) was monitored through a linear variable differential transducer (LVDT) which was connected to the bellows. To measure the reference density, the Micromeritics Helium Accupyc 1330™ pycnometer was used. The density of the exposed but uncured material was measured to be 1.3943 g/cm^3.

Isothermal experiments on the exposed but uncured material were conducted at 130 °C, 135 °C, and 145 °C. The lower isothermal cure temperatures were selected because too much coupling could occur between the initial thermal expansion and the onset of polymerization shrinkage at higher temperatures. The dilatometer was run in the "data acquisition mode," i.e., the specific volume was recorded against time. The specific volume data was then scaled by the respective sample weight, and the volume change (polymerization shrinkage) from the start of the isothermal segment till cool-down to room temperature was calculated, as shown in Fig. 8. The data set for the 135 °C run is incomplete due to some problems with the data acquisition mode. From these results, as well as the isothermal DSC results in Section II-A, one can determine that the polymerization (or chemical) shrinkage is very small (0.8% for DOC $\cong 40\%$ and 1.1% for DOC $\cong 60\%$). In addition, the CTE-induced volumetric shrinkage on cool-down was approximately 5–6% for samples cured 40–60%. The low shrinkage during polymerization is highly desirable in order to ensure the accuracy and registration of the fine interconnect features when aggressive design rules are pursued. Also, the low shrinkage is helpful in reducing the residual warpage and stresses.

To develop a cure-shrinkage model, the volumetric shrinkage was cross-plotted with DOC ([14]). However, no correlation could be established from the data at hand. This may be attributed to the aforementioned problem of coupling between the initial thermal expansion and onset of polymerization shrinkage. The coupling effects will be significant at the higher cure temperature of 145 °C, because the reaction rate might be much faster than the decrease in polymerization shrinkage at the beginning of the isothermal hold. On the other hand, conducting additional experiments at lower temperatures is not useful, since the maximum DOC achieved is very low, and therefore, the model would have no value in extrapolation of the polymerization shrinkage to a higher DOC.

IV. Thermomechanical Characterization

In this section, characterization of the following properties of Vialux™ 81 is presented:

1) coefficient of thermal expansion (CTE) of the fully cured material;
2) bulk modulus of the fully cured material;
3) stress relaxation modulus of the partially and fully cured material.

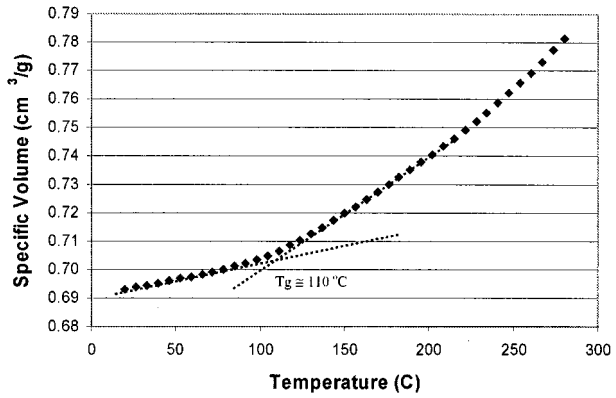
The thickness of the uncured thin film samples was 3 mils (76.2 μm). Isothermal cure at 175 °C for 1 h was done to obtain the fully cured samples.

The results from the PVT experiment on fully cured samples are presented first, and the temperature-dependent volumetric CTE and bulk modulus are derived from the PVT data. The GNOMIX™, Inc. PVT apparatus was run in isothermal mode from room temperature to 275 °C in 5 °C increments. At each isothermal temperature, the sample was subjected to a pressure compression cycle from 10–200 MPa in 10 MPa increments. The sample weight was 1.52 g, and the reference density as measured by the Micromeretics pycnometer was 1.4428 g/cm^3.

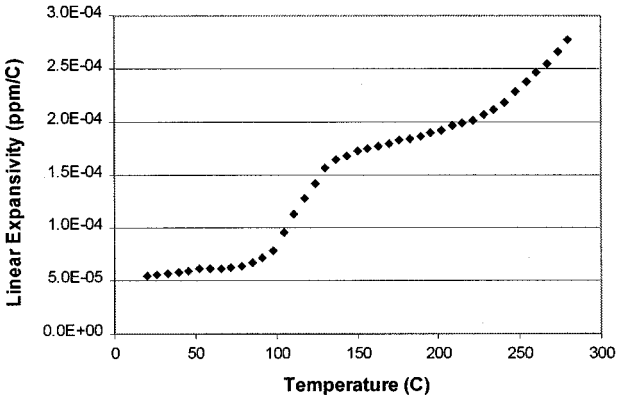
Shown in Fig. 9 is the variation of specific volume versus temperature, with the cross-plotted isobars. As opposed to fitting a modified 2-domain Tait equation of state ([15]), a piecewise interpolation scheme was used to compute the volumetric CTE (β) and bulk modulus (K) using the following expressions:

$$\beta(P,T) = \frac{1}{V}\left(\frac{dV}{dT}\right)_P \tag{5a}$$

$$B(P,T) = \frac{1}{K(P,T)} = -\frac{1}{V}\left(\frac{dV}{dP}\right)_T \tag{5b}$$



(a)



(b)

Fig. 10. (a) Specific volume versus temperature at 1 atmosphere (0.101 325 MPa) for the fully cured material and (b) variation of linear CTE with temperature.

where $B(P,T)$ is the compressibility. Note that the 0 MPa isobar curve is an extrapolated result, since a minimum pressure of 10 MPa is always maintained on the sample.

A. Coefficient of Thermal Expansion (CTE)

To determine the linear CTE (α) of the fully cured material, two measurement techniques were employed. The volumetric CTE (β) was determined from PVT experiments using (5a) and the data in Fig. 9. Assuming isotropic material behavior, which is a fairly good approximation for epoxy polymers, the linear CTE may be calculated using $\alpha = \beta/3$. In Fig. 10(a), the specific volume versus temperature curve at atmospheric pressure is illustrated. Using (5a) and dividing the data by 3, the linear CTE may be calculated, as shown in Fig. 10(b). The glass transition temperature, from Fig. 10(a) or 10(b), is at approximately 110 °C, which is consistent with that from DSC experiments ([4]) and DMA experiments (see Section IV-C). The large increase in CTE above the T_g is due to the softening of the material, i.e., significant plastic deformation will occur at temperatures above the T_g.

In fact, this softening behavior was more apparent when the linear CTE measurements were done using the TA Instruments Thermomechanical Analyzer™ (TMA) 2940 in film tension mode. A 3 g tensile load was applied on the sample, and a temperature scan rate of 5 °C/min was used. The value for the linear CTE below was comparable to the linear CTE

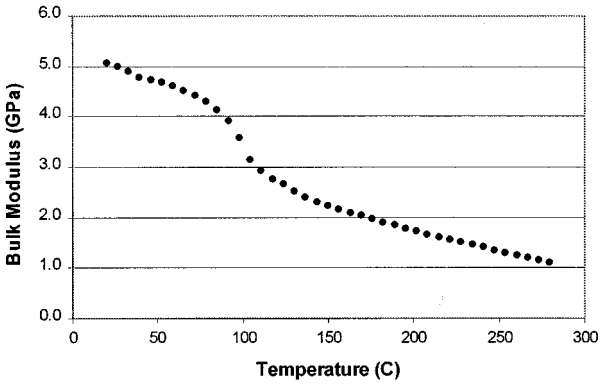


Fig. 11. Variation of bulk modulus with temperature.

calculated from the volumetric CTE data as in Fig. 10(b) (about 60 ppm/°C). However, above T_g, the abnormally large dimensional changes resulted in $\alpha = 525$ ppm/°C T_g (not shown in any figure) at $T = 140$°C, while the value from Fig. 10(b) is about 170 ppm/°C. This discrepancy is caused due to the tensile load applied on the sample, which accentuates the dimensional changes associated with the large scale plastic deformation above T_g (similar behavior as is observed in thermoplastics). Therefore, the linear expansivity based on the volumetric expansivity measurement was considered to be a more reliable estimate of the CTE, since the sample is purely under hydrostatic loading conditions.

B. Bulk Modulus $(K[T])$

The temperature-dependent bulk modulus of the fully cured sample is also a derived property from the PVT experiment. Equation (5b) is used to calculate K, and the temperature-dependence at atmospheric pressure is plotted in Fig. 11. The bulk modulus decreases by a factor of about 4.5 between room temperature and 275 °C, the largest change occurring around the glass transition temperature.

C. Cure-Dependent Stress Relaxation Modulus $(E[\alpha,t])$

The TA Instruments Dynamic Mechanical Analyzer™ (DMA) 2980 was used to conduct the viscoelastic stress relaxation experiments, with the thin film tension clamp. To prepare different DOC samples, (exposed) uncured films were cured at different isothermal temperatures (145 °C, 155 °C, 165 °C, and 175 °C). These temperatures corresponded to samples with a maximum DOC of 67, 77, 89, and 100%, respectively. The thin film samples were rectangular in shape, with a length of 25 mm and a width of 5 mm.

An initial screening experiment was done at room temperature on each of the samples, to assess the linear viscoelastic region. A controlled force experiment was conducted at a ramp rate of 0.1 N/min from 0 to 10 N to determine the stress-strain curve. At the maximum load of 10 N, the stress and the strain were 40 MPa and 1.5% respectively. From the initial linear segment in the stress–strain curve, the elastic modulus at room temperature was determined, and a strain of 0.2% was selected for conducting the stress relaxation experiments.

To determine the glass transition temperature of the samples cured to different DOC's, a dynamic temperature scan experi-

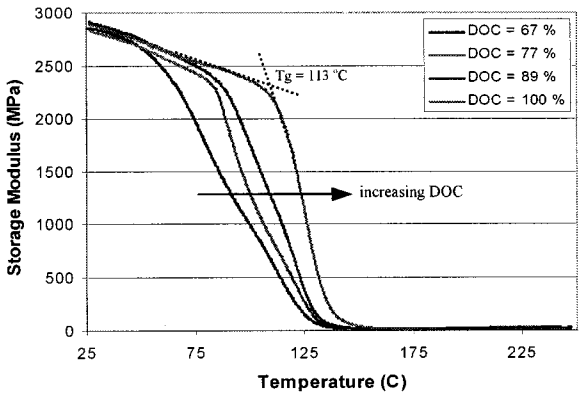


Fig. 12. DMA temperature scan at 1 Hz on variable DOC samples.

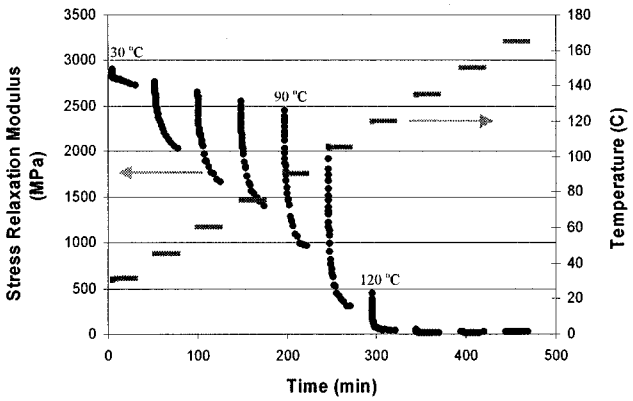


Fig. 13. Raw data of the stress relaxation test for the fully cured sample $(\mathrm{DOC} = 100\%)$.

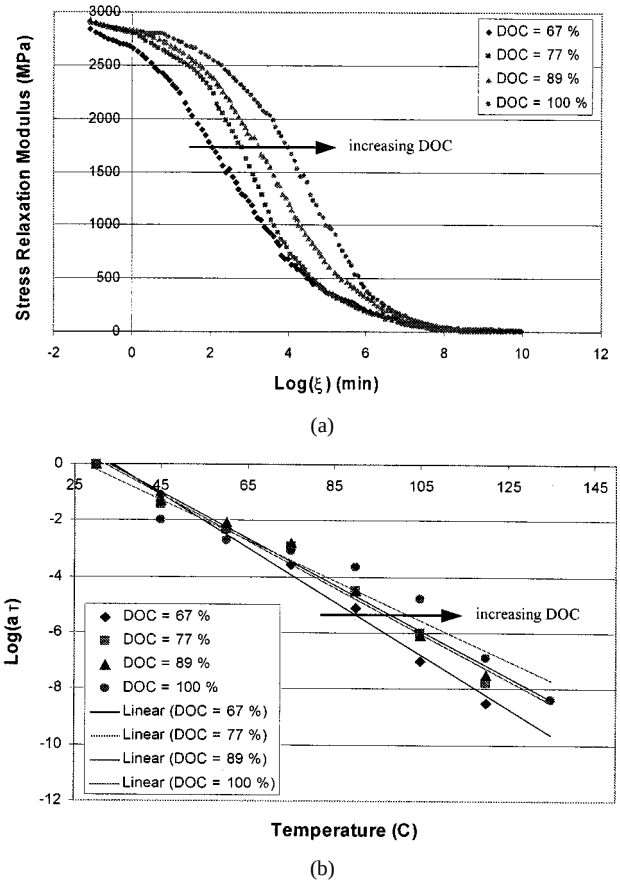


Fig. 14. (a) Master curves for the cure-dependent stress relaxation modulus and (b) shift functions used in the TTS to obtain the cure-dependent stress relaxation modulus master curves.

ment was conducted in film tension mode at 1 Hz, with a scan rate of 5 °C/min (Fig. 12). The step change in the storage modulus was used to locate the T_{g}, as this yields a value consistent with the PVT experiment. PVT experiments give the true thermodynamic glass transition, independent of rate effects. The T_{g} for samples with a DOC of 67, 77, 89, and 100% are 60, 83, 88, and 113 °C, respectively.

The T_{g} of the (exposed) uncured sample cannot however be measured using the DMA, as the material is extremely malleable at room temperature. Therefore, the TA Instruments modulated DSC (MDSC) instrument was used to measure the T_{g} from the step change in the reversible heat flow signal. The sample was heated from −60 °C to 150 °C with an underlying heating rate of 5 °C/min, a modulation amplitude of ±1 °C and a modulation period of 40 s. The T_{g} of the (exposed) uncured material was at 14 ± 2 °C, which explains why the uncured sample is so soft at room temperature.

For the stress relaxation testing, as selected earlier, a strain level of 0.2% was maintained. After clamping, the specimen was equilibrated at 30 °C for 5 min. The strain was kept constant at 0.2% for 30 min and the relaxed stress values were measured with time. A 10 min hold at this temperature was incorporated to allow for strain recovery. The temperature was then incremented by 15 °C, equilibrated for 5 min, and the procedure was repeated. The cure temperature was used as the upper limit to prevent any additional curing during the relaxation experiment. A low tensile static force of 0.005 N was imposed on the specimen at all times. Fig. 13 shows the raw stress relaxation modulus data for the fully cured case. This data is first re-plotted on a logarithmic (real) time axis. Subsequently, the data at each temperature is shifted horizontally to obtain a master curve using the time-temperature superposition (TTS) principle ([16]). Note that the abscissa is now the logarithm of the reduced time, ξ, which is given by

$$\xi = \int_{o}^{\mathrm{T}} \frac{1}{a_T(T)} dt \tag{6}$$

where a_T is the temperature shift function. Materials exhibiting this property are called thermo-rheologically simple (TRS). The reference temperature for the master curve was chosen to be 30 °C.

Shown in Fig. 14(a) and (b) are the stress relaxation modulus master curves and the associated shift functions for samples cured to different DOC's. As is to be expected, the sample cured to a lesser extent relaxes much faster as compared to the fully cured material [Fig. 14(a)], due to a decrease in the material relaxation time. The dramatic reduction in the relaxation modulus (about two decades) observed is due to the increase in molecular motions above the T_{g}. From Fig. 14(b), the logarithm of the shift functions was found to be linearly dependent on temperature, and the slope of this line decreased in magnitude with an increase in the DOC ([18]). In addition, the unrelaxed (glassy) and relaxed (rubbery) moduli for the different DOC cases were

found to be fairly constant. The constancy of the glassy modulus is because the molecular motions are so frozen-in below T_g, that the additional restriction of the cross-links is hardly noticeable.

Finally, a few experimental difficulties warrant further discussion and justification. When the stress relaxation experiments were conducted using partially cured samples, there was evidence of cure advancement during the course of the experiment. This was evident from the slight increase in the relaxation modulus at higher temperatures for partially cured specimens, and was confirmed by conducting a dynamic DSC at 10 °C/min on the samples at the completion of the stress relaxation experiment. Therefore, not all the stress relaxation data could be used for constructing the master curves. Another problem which was encountered during experimentation was the lack of complete strain recovery above the glass transition temperature in all the test cases. This was probably due to the excessive sample softening due to large scale plastic deformation ([17]), as was observed earlier in the linear CTE measurements. However, for all the test cases, above T_g, the stress relaxation modulus dropped rather rapidly (i.e., the material is almost in the rubbery relaxed state), which implies that the master curves in Fig. 14(a) are a reliable representation of the relaxation behavior for this material.

V. Conclusions

As seen from the dynamic DSC scans, the ViaLux™ 81 PDDF exhibits a complex curing mechanism. An increase in the UV exposure dose significantly reduces the curing cycle times. In fact, for samples exposed to 2000 mJ/cm^2, the isothermal DSC data suggested that a final thermal bake cure duration of approximately 15 min at temperatures above 165 °C could result in a DOC greater than 90%. A cure kinetics model was developed based on the isothermal data, to aid the optimization of the processing conditions for a wide range of potential applications and to understand the structure-property relationships. The predictive capability of the modified autocatalytic model with temperature-dependent kinetic parameters was fairly good for isothermal and dynamic heating conditions. Therefore, with due consideration to solvent and environmental (light, moisture, etc.) effects, and to the unavailability of material composition information, the cure kinetics model developed here is useful to monitor the DOC evolution. It can be used for typical isothermal cure conditions, as well as for complex cure schedules having combined heating rate and isothermal segments.

The cure shrinkage experiments confirm the low shrinkage observed in epoxy thermosets. This is desirable in order to realize the aggressive design rules in HDI substrate fabrication. However, the effort to develop a cure shrinkage model was unsuccessful due to the coupling between the initial thermal expansion and the onset of polymerization shrinkage at the beginning of the isothermal PVT experiments.

Besides investigating the curing process, a comprehensive characterization of the thermomechanical properties of the ViaLux™ 81 PDDF film was also undertaken. This involved the determination of the temperature-dependent CTE and bulk modulus, as well the cure-dependent stress relaxation modulus. Significant sample softening was observed for temperatures greater than the glass transition temperature ($T_g \cong 110\,°C$) due to large scale plastic deformation.

In conclusion, this work illustrates the complexity of the curing kinetics in photopolymer systems, as well as the difficulties with thermomechanical characterization of thin film materials. Nevertheless, the experimental characterizations are necessary to determine an appropriate processing strategy, and to obtain a consistent product with the desired physical and mechanical properties.

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Mookan Periyasamy, photograph and biography not available at the time of publication.

John Coburn, photograph and biography not available at the time of publication.